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# Magnetic resonance studies of defects in GaN with reduced dislocation densities

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## Abstract

Magnetic resonance experiments, including optically detected magnetic resonance (ODMR) and electron paramagnetic resonance (EPR), have been performed on Si-doped homoepitaxial GaN layers grown by MOCVD and on high quality, free-standing ( $\sim 200\text{ }\mu\text{m}$ -thick) GaN grown by HVPE. This allowed us to obtain information on the properties of native defects and dopants in GaN with a significantly reduced density of dislocations ( $< 10^7\text{ cm}^{-2}$ ) compared to that typically observed ( $\sim \text{mid } 10^8\text{--}10^{10}\text{ cm}^{-2}$ ) in conventional heteroepitaxial GaN layers. The high structural and optical quality of the layers was revealed by cross-sectional TEM and detailed low-temperature photoluminescence (PL) studies, respectively. ODMR at 24 GHz on strong shallow donor–shallow acceptor recombination from the Si-doped homoepitaxial layer reveals evidence for Si or C shallow acceptors on the N sites. EPR of the new free-standing HVPE GaN confirms the low concentration of residual donors ( $\sim 10^{16}\text{ cm}^{-3}$ ) as determined by Hall effect measurements. In addition, new deep centers are found from ODMR on the 2.4 eV “green” PL band and on the broad emission less than 1.8 eV from the HVPE GaN template. However, contrary to expectations, the reduction of random strain fields (associated with dislocations) has not led to significant changes in the character of the magnetic resonance (such as resolved electron-nuclear hyperfine structure) compared to that typically found for heteroepitaxial GaN layers. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** GaN; Homoepitaxial; Photoluminescence; Magnetic resonance; HVPE

## 1. Introduction

Dislocations are commonly thought to have a significant impact on the incorporation of impurities

and other point defects in GaN. Their influence on the electrical and optical properties of GaN and related alloys has been a subject of high interest. This includes their role as charged scattering centers and source of leakage paths in carrier transport in GaN materials and device structures [1,2]. Also, it has been suggested that radiative recombination processes such as the ubiquitous 2.2 eV “yellow” emission band occurs at or near dislocations [3].

The high levels of dislocations ( $\sim \text{mid-}10^8\text{--}10^{10}\text{ cm}^{-2}$ ) typically found in conventional GaN heteroepitaxial layers are often thought to compromise the identification of residual defects and to influence the spin properties of dopants as investigated through magnetic

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resonance techniques. For example, random strain fields associated with the dislocations can strongly influence the spin properties of shallow acceptors derived from degenerate or nearly degenerate valence band states. Also, as a source of additional broadening, these strain fields can render electron-nuclear hyperfine structure unobservable.

In order to explore these issues, low-temperature photoluminescence (PL), electron paramagnetic resonance (EPR), and optically detected magnetic resonance (ODMR) have been performed on homoepitaxial GaN layers grown by MOCVD and on high-quality, free-standing (thick) GaN grown by HVPE. This allowed us to obtain information on the properties of native defects and dopants in GaN with dislocation densities at least 2–3 orders of magnitude smaller than usually observed for GaN deposited on  $\text{Al}_2\text{O}_3$  or 6H-SiC substrates. Several new defects are revealed from these studies, including evidence for either shallow Si or C acceptors on the N sites in the GaN homoepitaxial layers and for new deep centers in the HVPE-grown GaN. However, contrary to expectations, the reduction of random strain fields (associated with the dislocations) has not led to significant changes in the character of the magnetic resonance compared to that typically found for conventional heteroepitaxial GaN [4–7].

## 2. Experimental background

PL and ODMR experiments were performed on GaN homoepitaxial layers grown by MOCVD on the (0001) Ga face of (unintentionally doped) GaN bulk crystals. More details on the high pressure–high temperature synthesis of these crystals and the particular treatment of the surfaces prior to deposition of the CVD layers are provided elsewhere [8–9]. In this work the PL and ODMR from a 1  $\mu\text{m}$ -thick Si-doped ( $\sim 1\text{--}2 \times 10^{17} \text{ cm}^{-3}$ ) GaN homoepitaxial layer are highlighted. This film was deposited on top of 5  $\mu\text{m}$  of undoped MOCVD-grown GaN. Cross-sectional TEM measurements revealed the high structural quality of these undoped and Si-doped homoepitaxial layers with dislocation densities  $< 10^7 \text{ cm}^{-2}$ . However, it is possible that the dislocation densities are significantly lower as observed from defect selective etching experiments [10] of similar homoepitaxial layers grown on these GaN bulk crystals.

PL, EPR, and ODMR were also performed on thick ( $\sim 200 \mu\text{m}$ ) free-standing (n-type) GaN grown by HVPE after laser-assisted liftoff from the parent 2 in dia.  $\text{Al}_2\text{O}_3$  substrate [11]. We note that the ODMR was obtained on PL from the top (growth-surface) side of this material which was mechanically polished and reactive ion etched. Recent X-ray, AFM, TEM, and Raman scattering measurements [11–14] all indicate the high crystalline quality of this HVPE GaN. In particular, similar to that

found for the GaN homoepitaxial layers, dislocation densities  $< 10^7 \text{ cm}^{-2}$  were revealed by TEM images [11]. Furthermore, variable-temperature Hall effect measurements [12,15] on samples from the same wafer or ones similar to those investigated in this work revealed remarkably low levels of residual shallow donors ( $\sim 7 \times 10^{15}\text{--}1.2 \times 10^{16} \text{ cm}^{-3}$ ) and compensating acceptors ( $\sim 2\text{--}3 \times 10^{15} \text{ cm}^{-3}$ ) and, in addition, the highest low-temperature electron Hall mobilities ( $\sim 8000 \text{ cm}^2/\text{Vs}$ ) attained to date in bulk GaN.

High-resolution PL was obtained at 5 K with the 325 nm line from a He–Cd laser. This emission was analyzed by a 0.85-m double-grating spectrometer and detected by a GaAs PMT. The PL between 1.3 and 3.3 eV was also obtained at 1.6 K under the same photoexcitation conditions as employed in the ODMR experiments. This PL was generated by the 351 nm line from an  $\text{Ar}^+$ -ion laser ( $\sim 1 \text{ W/cm}^2$ ), analyzed by a 0.22-m double-grating spectrometer, and detected by a Si photodiode. The 9.5 GHz EPR and 24 GHz ODMR spectrometers used in this work are described elsewhere [5].

## 3. Results and discussion

### 3.1. GaN homoepitaxial layers

As observed by other groups [16–18], high-resolution PL studies confirmed the high-crystalline quality of our undoped and Si-doped GaN homoepitaxial layers [19]. In particular, the Si-doped homoepitaxial sample exhibits sharper excitonic PL (linewidths  $\leq 1 \text{ meV}$ ) compared to that reported previously for GaN grown on  $\text{Al}_2\text{O}_3$  with similar Si doping levels [20]. The PL below 3.4 eV from the Si-doped homoepitaxial layer is shown in Fig. 1. Strong recombination at 3.26 eV and a series of LO phonon replicas ( $E_{\text{LO}} \sim 92 \text{ meV}$ ) at lower energies are observed. This emission shifts monotonically to lower energies with decreasing excitation power densities ( $\sim 11 \text{ meV}$  with  $P_{\text{exc}}$  reduced from 1 to  $0.001 \text{ W/cm}^2$ ). Based on these characteristics and previous work [21], this PL is attributed to a recombination between shallow Si donors ( $E_{\text{d}} \sim 30 \text{ meV}$ ) and shallow acceptors ( $E_{\text{a}} \sim 220 \text{ meV}$ ). Likely candidates for the shallow acceptors will be discussed shortly. In addition, as invariably observed to some degree of strength in most n-type (as-grown or Si-doped) CVD GaN [5], a broad “yellow” PL band at 2.2 eV is also found. No additional emission was observed from this layer between 1.3 and 1.8 eV.

The ODMR obtained on the 2.2 eV PL band from the Si-doped GaN homoepitaxial layer with  $\mathbf{B} \perp c$  is shown in Fig. 2. For comparison, ODMR on similar emission from (n-type) heteroepitaxial GaN reference layers grown on  $\text{Al}_2\text{O}_3$  [5] and 6H-SiC [22] is also provided.

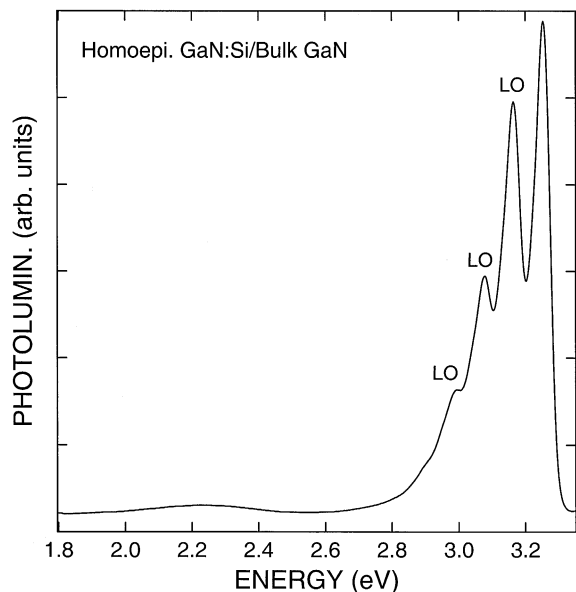


Fig. 1. PL obtained below 3.4 eV at 1.6 K from the Si-doped GaN homoepitaxial layer with  $\sim 1 \text{ W/cm}^2$  of 351 nm radiation.

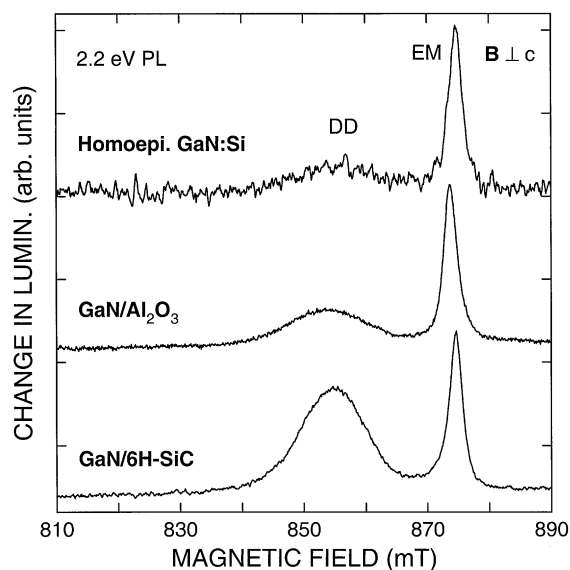


Fig. 2. ODMR spectra found at 24 GHz on the 2.2 eV “yellow” PL bands from the Si-doped homoepitaxial GaN layer and heteroepitaxial GaN layers grown on  $\text{Al}_2\text{O}_3$  and 6H-SiC (EM  $\equiv$  effective-mass donor, DD  $\equiv$  deep defect).

The lower signal-to-noise ratio of the ODMR from the homoepitaxial layer (as also seen in Fig. 3) relative to that found for the reference samples mainly reflects the degradation of the microwave cavity mode due to the high conductivity of the bulk GaN substrate. However, it is clear that the character of the ODMR observed on

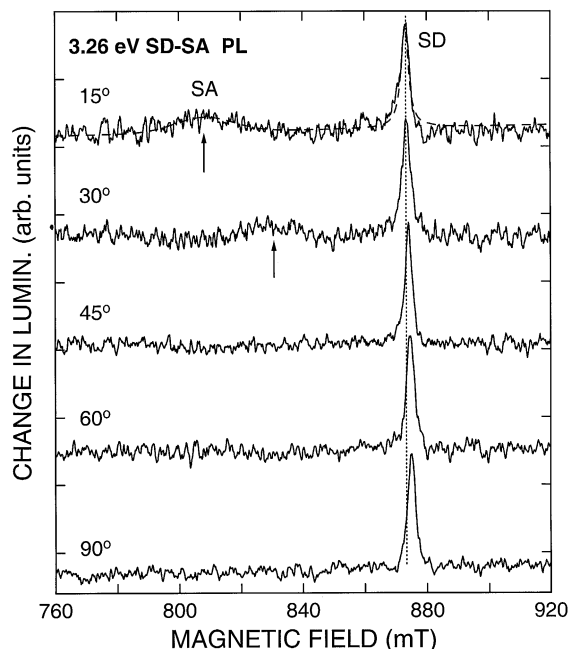


Fig. 3. ODMR obtained on the 3.26 eV SD-SA PL from the homoepitaxial GaN:Si film. The dashed curve is a two-component fit of the spectrum with  $\mathbf{B}$   $15^\circ$  from the  $c$ -axis. The dotted line indicates the position of the SD resonance with  $\mathbf{B}$  near the  $c$ -axis.

this emission in the three cases is quite similar. Unfortunately, in spite of the reduced level of dislocations, no resolved hyperfine structure could be observed in the magnetic resonance of the homoepitaxial layer. The sharp feature (FWHM  $\sim 2\text{--}3 \text{ mT}$ ) with  $g_{\parallel} = 1.952$  and  $g_{\perp} = 1.949$  is assigned to (effective-mass) shallow donors based on the previous work [4,5]. The shallow donors are likely Si on the Ga sites although residual O on the N sites may also contribute to part of this signal based on recent evidence for the shallow nature of O impurities in GaN [23]. Most groups agree that the broad resonance (FWHM  $\sim 15 \text{ mT}$ ) with  $g_{\parallel} = 1.989$  and  $g_{\perp} = 1.992$  is associated with a deep defect (DD). We first ascribed this feature to deep donors based, in part, on the small negative  $g$ -shift with respect to the free electron  $g$ -value of 2.0023 [5]. However, from a magnetic resonance standpoint, the donor or acceptor character of this center is an open question based on the observation of similar  $g$ -shifts for one of the extremal  $g$ -values (i.e.,  $g_{\perp}$ ) associated with shallow Mg acceptors in GaN [24,25].

Representative ODMR found on the strong 3.26 eV SD-SA PL from the Si-doped GaN homoepitaxial film is shown in Fig. 3. Two luminescence-increasing signals are observed. The first feature (labeled SD) is again attributed to shallow donors based on the resonance

parameters (i.e.,  $g_{\parallel}$ ,  $g_{\perp} \sim 1.95$ ). The second line (labeled SA) is only observed above the background for  $\mathbf{B} < 45^\circ$  from the  $c$ -axis. However, if we take this limited data set and the usual expression for the  $g$ -values in the case of axial symmetry that describes most of the magnetic resonance observed to date in GaN (i.e.,  $g(\theta) = (g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2}$ , where  $\theta$  denotes the angle between  $\mathbf{B}$  and the  $c$ -axis), the extremal  $g$ -values for this resonance are  $g_{\parallel} \sim 2.1$  and  $g_{\perp} \sim 1.99$ .<sup>4</sup> Most notably, this  $g$ -tensor is quite similar to that found from EPR and ODMR of shallow Mg acceptors in heteroepitaxial Mg-doped GaN [23,24]. For example, a comparison of the ODMR found on the SD-SA emission from the homoepitaxial layer with that observed on equivalent emission from a Mg-doped GaN/Al<sub>2</sub>O<sub>3</sub> heteroepitaxial layer with  $[\text{Mg}] \sim 2.5 \times 10^{18} \text{ cm}^{-3}$  (grown in a separate CVD reactor) is shown in Fig. 4. Thus, based on the similar character of the PL bands and the magnetic resonance, the broad ODMR feature on the 3.26 eV PL from the Si-doped homoepitaxial layer is assigned to shallow acceptors.

We note that Mg had never been introduced as a dopant source in the reactor employed for the growth of these homoepitaxial layers. Thus, we propose that likely candidates for the residual shallow acceptors are C or Si on the N lattice sites. The amphoteric nature of Si and C has been established for other III–V semiconductors such as GaAs [26]. In addition, recent PL work suggests that Si also introduces an acceptor level in GaN with  $E_a$

of  $\sim 220 \text{ meV}$  [27]. Thus, this feature (SA) is tentatively assigned to Si<sub>N</sub> shallow acceptors, but we can not rule out C<sub>N</sub> being responsible for all or part of this signal. Additional work is underway to identify this defect [19].

The apparent loss of the shallow acceptor resonance in the homoepitaxial layer for  $\theta \geq 45^\circ$ , perhaps due to severe broadening, is not understood at this time. We note, however, that similar intensity behavior and broadening (though not to the same degree) are often observed from magnetic resonance of (effective-mass) shallow acceptors and holes with highly anisotropic  $g$ -tensors (i.e.,  $g(\theta) = g_{\parallel} \cos(\theta)$ ,  $g_{\parallel} \sim 2-4$ ,  $g_{\perp} \sim 0$ ) associated with the  $m_j = \pm 3/2$  (heavy-hole) valence band in other semiconductors such as bulk 6H-SiC [28] and CdS [29] and SiGe quantum wells under tensile strain [30]. For such states, any inhomogeneity in  $g_{\parallel}$  will lead to a pronounced broadening of the resonance when  $g(\theta)$  is rapidly changing as is the case with  $\theta \geq 45^\circ$ .

Finally, we note that the nearly isotropic  $g$ -tensor associated with the shallow acceptors in the Si-doped homoepitaxial GaN layer is quite different than the highly anisotropic  $g$ -tensor expected (given above) for such centers in WZ GaN from effective-mass theory [31]. This likely reflects a symmetry-lowering local distortion of the shallow acceptors. Overall, the present results suggest that (a) the non-effective mass like character is not specific to Mg<sub>Ga</sub> shallow acceptors and (b) random strain fields associated with high dislocation densities do not appear to be the major source of perturbation responsible for the nearly isotropic  $g$ -tensors observed for shallow acceptors in conventional heteroepitaxial GaN.

### 3.2. Free-standing (thick) HVPE GaN

Though not nearly as sharp as the excitonic PL observed from undoped GaN homoepitaxial layers with linewidths of  $\sim 0.1 \text{ meV}$  [16–19], the bandedge emission from these free-standing (thick) HVPE GaN templates is characterized by linewidths less than  $1 \text{ meV}$  [14]. An example of a high-resolution PL spectrum obtained at 5 K that demonstrates the high crystallinity of this material is shown in the inset of Fig. 5. Both impurity-bound and free exciton lines are observed between 3.46 and 3.52 eV [14]. The PL below 3.3 eV from this sample is also shown in Fig. 5. Most notably, instead of the 2.2 eV “yellow” PL band, a broad “green” emission band at 2.4 eV is found. Recent lapping studies [13] of these templates with  $\sim 15 \mu\text{m}$  removed from the

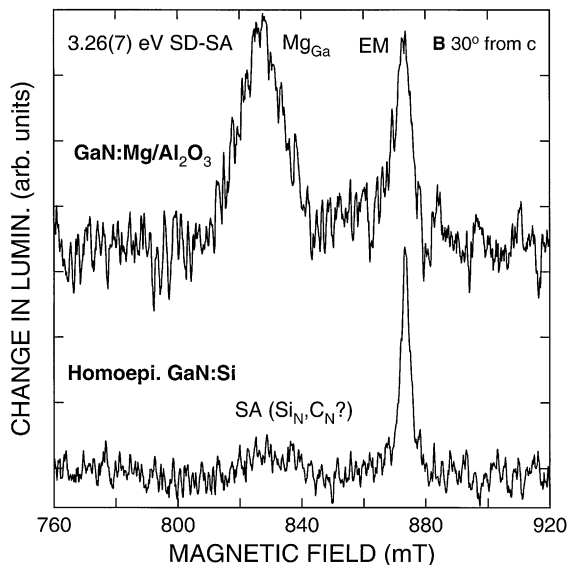


Fig. 4. Comparison of the ODMR observed on the SD-SA PL bands from a Mg-doped GaN/Al<sub>2</sub>O<sub>3</sub> sample (from Ref. [24]) and the Si-doped GaN homoepitaxial layer. The emission from the Mg-doped GaN layer was analyzed through a 0.22 m double-grating spectrometer.

<sup>4</sup> We note that the highly anisotropic expression expected for the  $g$ -tensor (i.e.,  $g(\theta) = g_{\parallel} \cos(\theta)$ ,  $g_{\perp} \sim 0$ ) of effective-mass shallow acceptors in WZ GaN (as found for shallow acceptors in other semiconductors with similar hexagonal crystal symmetry such as 6H-SiC and CdS) does not describe the  $g$ -values of this resonance.

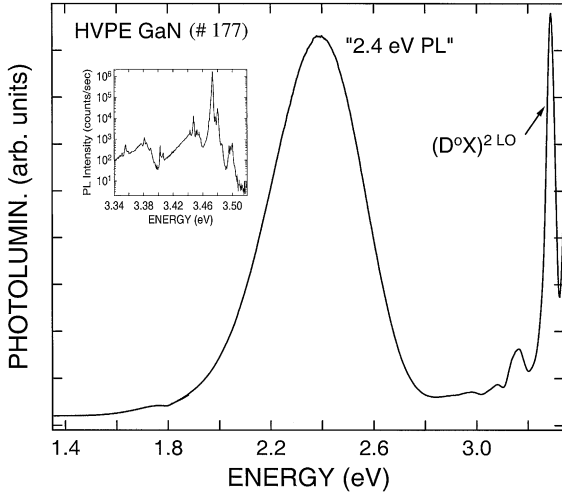


Fig. 5. PL spectrum obtained below 3.3 eV at 1.6 K from the free-standing HVPE GaN template. The small dip near 1.8 eV is a grating response. Inset: high resolution PL found at 5 K in the near-bandgap spectral regime (from Ref. [14]).

damaged back surface indicate that this emission is intrinsic to the bulk material (i.e., not a result of the post-growth treatment). One group has proposed that isolated Ga vacancies ( $V_{\text{Ga}}$ ) or  $V_{\text{Ga}}$ -related complexes are involved in this “green” PL [32]. In addition, as typically observed from HVPE-grown GaN [33,34], this sample exhibits weak, broad emission between 1.4 and 1.8 eV (referred to as the “red” PL band).

A representative EPR spectrum obtained for the 170  $\mu\text{m}$ -thick GaN template with  $\mathbf{B} \perp c$  is shown in Fig. 6. The EPR for a 10  $\mu\text{m}$ -thick HVPE-grown GaN/ $\text{Al}_2\text{O}_3$  reference sample with  $n_{300\text{ K}} \sim 1 \times 10^{17} \text{ cm}^{-3}$  is also shown for comparison. Single lines with  $g_{\parallel}, g_{\perp} \sim 1.95$  are found and ascribed to shallow donors as discussed earlier. Most notably, the density of spins associated with the signal from the Samsung sample is estimated to be  $\sim 6 \times 10^{15} \text{ cm}^{-3}$  ( $\pm 50\%$ ) from a comparison with the EPR of a P-doped Si standard. This density is in good agreement with the concentration of uncompensated shallow donors ( $N_{\text{D}} - N_{\text{A}}$ ) determined from variable-temperature Hall effect measurements of samples from the same 2 in.-dia. wafer.

Unfortunately, additional structure was not revealed in the EPR of the Samsung HVPE GaN. In fact, due to a lower concentration of donors, this sample exhibits a broader EPR linewidth (FWHM  $\sim 27 \text{ G}$ ) compared to that found for the more highly conducting GaN/ $\text{Al}_2\text{O}_3$  layer (FWHM  $\sim 12 \text{ G}$ ) due to unresolved hyperfine structure between the spin of the (isolated) donors and the host lattice nuclei. This interaction is “averaged” out for GaN with larger concentrations of interacting

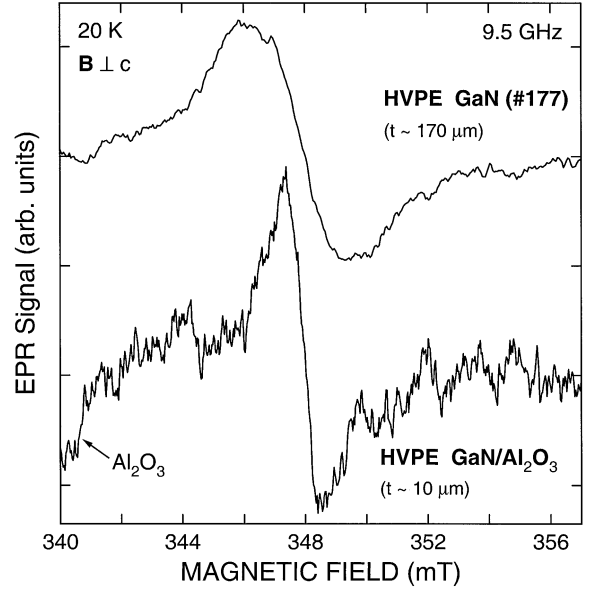


Fig. 6. EPR spectra obtained at 9.5 GHz for two HVPE-grown GaN samples. Top: free-standing GaN template ( $n_{300\text{ K}} \sim 1 \times 10^{16} \text{ cm}^{-3}$ ). Bottom: GaN/ $\text{Al}_2\text{O}_3$  reference;  $n_{300\text{ K}} \sim 1 \times 10^{17} \text{ cm}^{-3}$ .

donors [35] as found in the 10  $\mu\text{m}$ -thick HVPE GaN/ $\text{Al}_2\text{O}_3$  sample.

ODMR obtained on the 2.4 eV “green” PL band is shown in the top half of Fig. 7. As also found on the 2.2 eV “yellow” PL emission, the resonance labeled EM is assigned to effective-mass (shallow) donors. The second resonance, labeled  $A_1$ , is new. It exhibits a strong intensity anisotropy with  $g_{\parallel} = 1.975$  and  $g_{\perp} = 1.969$ . The  $g$ -values suggest a donor-like defect but the (axial) intensity anisotropy is more often found for acceptor-like defects associated with degenerate or nearly degenerate valence band states. Thus, though more work is clearly needed, we tentatively assign this feature to a deep acceptor of unknown origin. In addition, the  $g$ -tensor and intensity behavior of this center are quite different compared to that found for the deep defects (i.e.,  $g_{\parallel} = 1.989$  and  $g_{\perp} = 1.992$ ) involved in the 2.2 eV “yellow” PL [5–7,22]. This indicates that these centers are of different origin.

ODMR found on the PL less than 1.8 eV is shown in the bottom half of Fig. 7. Two luminescence-increasing signals are observed. The first line at  $\sim 870 \text{ mT}$  is again attributed to shallow donors. The second feature (labeled  $A_2$ ) is also new. It is isotropic with  $g = 2.019$  and a FWHM of  $\sim 25 \text{ mT}$ . This signal is assigned to deep acceptors based on these magnetic resonance parameters and the near-midgap PL. We note that this defect is different than the deep center with  $g_{\parallel} = 2.008$

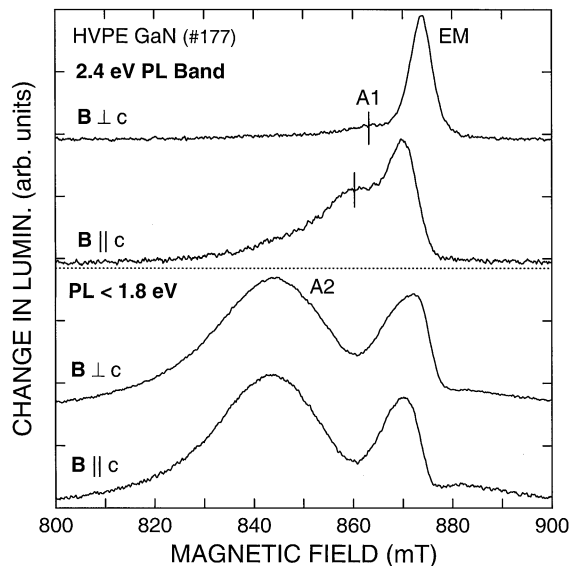


Fig. 7. ODMR found on the 2.4 eV “green” PL band and near-IR emission from the free-standing HVPE GaN sample. The features labeled  $A_1$  and  $A_2$  are tentatively assigned to acceptor-like defects.

and  $g_{\perp} = 2.004$  revealed by ODMR on similar near-IR emission from other HVPE-grown GaN [25,36].

#### 4. Summary

ODMR and EPR experiments have been performed on Si-doped homoepitaxial GaN layers grown by MOCVD and on free-standing (thick) GaN grown by HVPE. The high structural and optical quality of these materials was revealed by cross-sectional TEM and low-temperature PL studies, respectively. ODMR reveals several new defects, including evidence for either Si or C shallow acceptors on the N lattice sites in a Si-doped GaN homoepitaxial layer and for two new deep centers in the HVPE-grown GaN templates. In addition, EPR confirmed the low concentration of residual donors in these free-standing layers. The reduced dislocation densities, however, has not led to significant changes in the character of the magnetic resonance (such as resolved electron-nuclear hyperfine structure) compared to that found previously for conventional heteroepitaxial GaN. However, we suggest that the application of more sophisticated magnetic resonance techniques such as electron-nuclear double resonance (ENDOR) or optically detected—ENDOR should be pursued for identification of defects in these more pure GaN materials.

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